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**EFFECT OF POLLUTANT GASES ON OZONE PRODUCTION  
BY SIMULATED SOLAR RADIATION**

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# EFFECT OF POLLUTANT GASES ON OZONE PRODUCTION

## BY SIMULATED SOLAR RADIATION

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### INTRODUCTION

The present investigation provides some information related to the problem of ozone destruction by nitric oxide, NO, emission from high flying vehicles. According to Johnston (1971) and Westenberg (1972), NO emission could catalytically destroy ozone, O<sub>3</sub>, in the upper atmosphere to such an extent that additional ultraviolet, u.v., radiation would reach the earth with possible harmful effects.

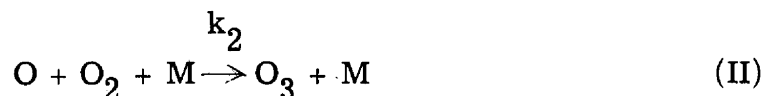
F. E. Belles of this Center suggested that if Johnston and Westenberg had included certain photochemical smog reactions in their NO-O<sub>3</sub> destruction scheme, NO destruction of O<sub>3</sub> might be reduced. Rapid NO conversion to nitrogen dioxide, NO<sub>2</sub>, followed by production of O<sub>3</sub>, has been observed in smog chamber experiments and Los Angeles smog (Leighton (1961)). This rapid NO conversion process to NO<sub>2</sub> followed by O<sub>3</sub> production is now believed to be a chain reaction involving unsaturated hydrocarbon and/or carbon monoxide, CO, oxidation (Leighton (1961), Heicklen et al. (1969), Westberg and Cohen (1971)). Thus, if engine exhausts have insufficient amounts of unsaturated hydrocarbon and CO to counteract the destruction of O<sub>3</sub> by the NO emitted, additional appropriate amounts of unsaturated hydrocarbon and/or CO could be added to engine exhaust gases.

Based on Belles' recommendation, experiments were conducted using simulated solar radiation in a chamber with controlled atmosphere. Pressure was near 1 atmosphere in these tests. Tests were made to evaluate NO destruction of O<sub>3</sub> in the chamber and to determine if addition of CO and H<sub>2</sub>O could reduce NO destruction of O<sub>3</sub>. In conjunction with these experiments, the General Chemical Kinetics Program (Bittker and

Scullin (1972)) developed at the Lewis Research Center was modified and extended to permit a detailed kinetics data analysis.

### CHEMICAL BACKGROUND

When pure air is irradiated with ultraviolet light, the formation of  $O_3$  is controlled chemically by the Chapman mechanism, as represented by the following reactions:



The recombination reaction  $O + O + M \rightarrow O_2 + M$  also occurs, but is of negligible importance at atmospheric and stratospheric conditions. In this discussion we neglect the formation of excited state species in the photolysis reactions. If it is assumed that oxygen atom concentration rapidly reaches a steady state value, then one can derive a differential equation for  $O_3$  production in which all terms containing  $J_3$  are negligibly small. This equation can be integrated to give the following expression

$$[O_3] = \frac{\nu_2}{k_4} \left[ 1 - e^{-\left( \frac{k_4 J_1 t}{k_2 [M]} + \frac{k_4 [O_3]}{2 \nu_2} \right)} \right] \quad (1)$$

where

$t$  = reaction time

$[O_3]$  = molar  $O_3$  concentration

$[M]$  = total molar concentration

$$\nu_2 = k_2[O_2][M]$$

In the expression  $e^{-x}$ , the exponent  $x$  is smaller than 0.1 for reaction times up to about 1000 hours, so that the expansion

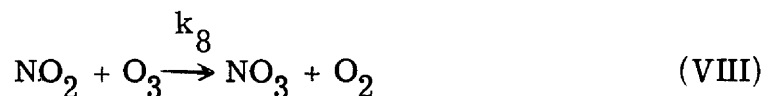
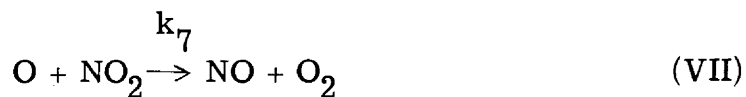
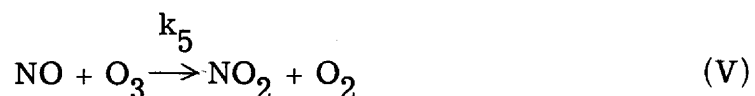
$$e^{-x} \cong 1 - x$$

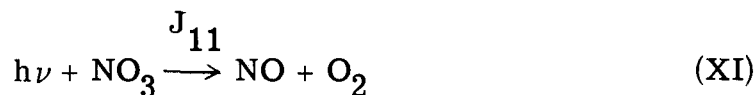
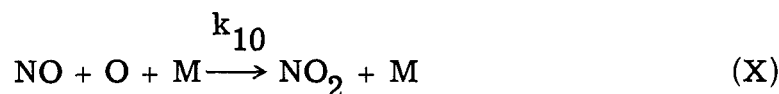
can be used. When this is done, the above equation becomes

$$[O_3] = 2J_1[O_2]t \quad (2)$$

Therefore, when pure air is irradiated,  $O_3$  concentration should rise linearly for a long time. The rate of rise is determined only by the rate of photolysis of  $O_2$  to form oxygen atoms.

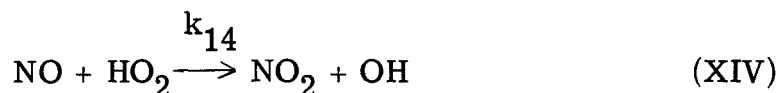
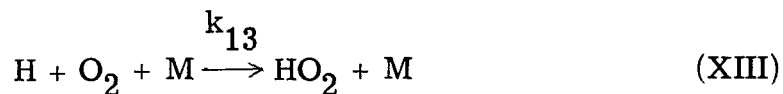
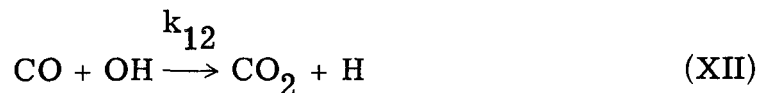
When dry air is irradiated in the presence of oxides of nitrogen, the following additional reactions occur which tend to destroy  $O_3$ :

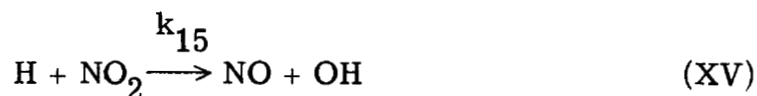




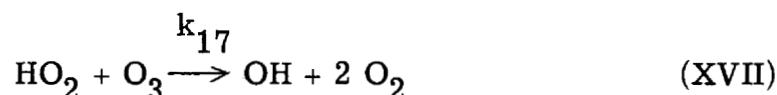
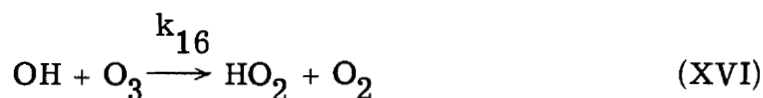
Johnston (1971) and Westenberg (1972) present steady-state mathematical analyses with the above mechanism. They show that the final  $\text{O}_3$  concentration level is indeed much lower than it is when oxides of nitrogen are not present. However, in assessing the effect of pollutants injected into the atmosphere, it is necessary to obtain the time variation of  $\text{O}_3$  concentration from the instant of injection. To obtain such concentration profiles the chemical mechanism must be numerically integrated. To perform this kind of computation, a general chemical kinetics program was developed several years ago at the Lewis Research Center (Bittker and Scullin (1972)). It has recently been expanded and improved to allow the inclusion of more types of reactions, including photochemistry and to make the integration method more efficient. This program has been used extensively in the present work to analyze and interpret the experimental results.

As mentioned previously the presence of  $\text{H}_2\text{O}$  and  $\text{CO}$  in jet engine exhaust gases gives rise to a series of reactions which may counteract the destruction of ozone (Heicklen et al. (1969)).



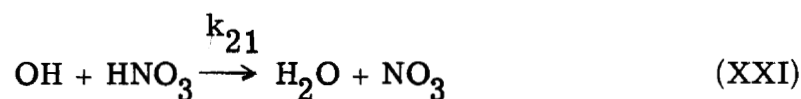
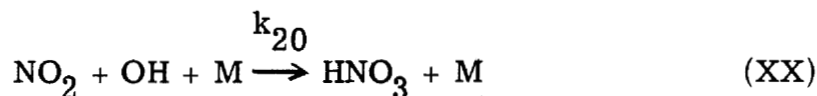
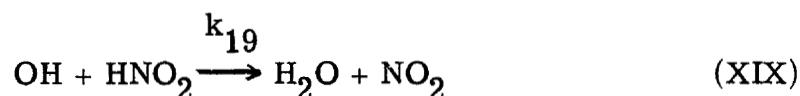
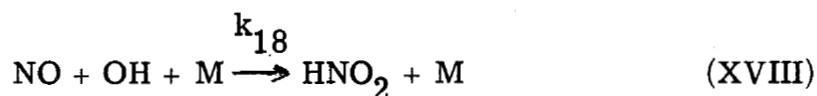


Reactions XII through XIV are quite fast and provide a strong competitive path for the conversion of NO to NO<sub>2</sub> without the destruction of O<sub>3</sub>. Reaction XV, which could regenerate NO, was found to be unimportant under our experimental conditions. One must also consider the possible destruction of O<sub>3</sub> in the presence of H<sub>2</sub>O alone, according to the chain mechanism:



The net effect of these last reactions is the conversion of two molecules of O<sub>3</sub> to three molecules of oxygen. In fact, H<sub>2</sub>O and not NO was originally thought to be the main destroyer of O<sub>3</sub> in engine exhaust gases (Kellogg (1970)). The most recent information on the values of  $k_{16}$  and  $k_{17}$  indicates that they are much smaller than originally estimated (Garvin and Hampson (1974) and DeMore (1973)). The destruction of O<sub>3</sub> by NO is now considered much more important than its destruction by the water mechanism. Nevertheless the mechanism of reactions XVI and XVII cannot be ignored when studying atmospheric chemistry. The effect of water on O<sub>3</sub> production has been studied briefly in the present work.

The formation of nitric and nitrous acids, HNO<sub>3</sub> and HNO<sub>2</sub>, has been suggested by many people as a means of removing NO from the stratosphere and thus reducing its destructive effect on ozone (Crutzen (1972), DeMore (1973), Dütsch (1972)). The possible formation of these species in the gas phase during the present work was checked by theoretical computations using these additional reactions:



## APPARATUS AND MATERIALS

The main apparatus for this experimental work consists of a chamber, a solar simulator, and instrumentation for monitoring  $\text{O}_3$  and  $\text{NO}_x$  ( $\text{NO}$  and  $\text{NO}_2$ ) concentrations.

### Reaction Chamber

An existing chamber at this Center was modified to permit addition of pollutant gases and gas sampling (Fig. 1). The chamber has a volume of about 650 liters (23 cu ft) with approximate dimensions of 82 cm ( $32\frac{1}{4}$  in.) inside diameter, and length of 122 cm (48 in.). Radiation enters the chamber through a 30.5 cm (12 in.) diameter quartz window at one end. In front of this window is a water cooled shutter so that radiation can be turned "on" or "off" instantly. This chamber can be evacuated to the low  $10^{-6}$  torr range using a 30.5 cm (12 in. dia.) oil diffusion pump fitted with a liquid nitrogen cold trap. The inside chamber surface is stainless steel. The radiation, after passage through the 30.5 cm window, is a slightly diverging beam inside the chamber, as shown in Fig. 1. At the opposite end of the chamber the radiation describes a light circle of about 40.6 cm (16 in.) in diameter. This indicates that about one-fifth of the effective chamber volume was exposed

to the radiation. Two Teflon sampling probes were positioned to sample gas in the center of the light beam in the chamber (Fig. 1).

### Solar Simulator

Simulated solar radiation was provided by a commercial solar simulator. With the apparatus shown in Fig. 1, the amount of  $O_3$  produced in the chamber when dry clean air is irradiated, depends to a large extent on the type of xenon arc lamp used. Three types of 4.2 kW xenon high pressure arc lamps - I. T. T., Ushio, and Osram - compatible with our solar simulator were tested. The peak  $O_3$  production in pphm was as follows:

	<u>pphm</u>
I. T. T.	20-30
Ushio	40-60
Osram	120-140

Due to its much higher  $O_3$  production, an Osram lamp was used throughout this study. According to the manufacturer such lamps will provide u. v. radiation beginning at about 200 nm. In the visible range its radiation is comparable to that emitted by the sun. Ultraviolet transmission through the quartz window was measured only as low as 250 nm, but it is possible that some radiation as low as 200 nm is also present in the transmitted light.

### Analytical Instruments

For this work two types of commercially available chemiluminescence analyzers were used to monitor  $O_3$  and  $NO_x$  ( $NO + NO_2$ ). Both instruments can only be used to sample at or near atmospheric pressure condition (low pressure limit  $\sim 700$  torr). Because of this limitation the work reported here was obtained for the near atmospheric pressure condition only.



### Test Gases

Clean dry air used in the irradiation experiment was commercially available tanked ultrapure clean ("UPC") air. This "UPC" air generally has the following typical stated analysis for contaminants in ppm by volume:

CO <sub>2</sub>	0.5	N <sub>2</sub> O (nitrous oxide)	0.1
CO	1.0	Total hydrocarbon	0.1
CH <sub>4</sub> (methane)	1.0	H <sub>2</sub> O	≤ 1.0

Desired amounts of H<sub>2</sub>O were added to "UPC" air by saturating the air with distilled H<sub>2</sub>O at some pre-selected low temperature just prior to its entry into the chamber.

Two other tanked gases were used. A mixture of NO (18 ppm) in nitrogen was used to calibrate the NO<sub>x</sub> analyzer and to introduce NO gas into the chamber. CO had a stated purity of 99.5 percent, and mass spectrometer analysis indicated that the 0.5 percent impurity in CO was mainly CO<sub>2</sub>.

## EXPERIMENTAL RESULTS

### Evaluation of Apparatus for Ozone Production

For the O<sub>3</sub> production tests the tank is first pumped to the low 10<sup>-6</sup> torr range for about a 20 hour period. Then "UPC" air is used to fill the tank to near atmospheric pressure. At time "zero," irradiation of this air is begun by removal of the shutter over the quartz window. The O<sub>3</sub> concentration in the tank is monitored as a function of time. Two O<sub>3</sub> production tests were made in succession on the same day, and these are shown in Fig. 2 where O<sub>3</sub> concentration in pphm is plotted against irradiation time in minutes. During these tests the chamber surface had not been exposed to any pollutant gases such as CO, NO<sub>x</sub>, or H<sub>2</sub>O. For the two runs it is interesting to note that O<sub>3</sub> production for the second run was much more regular. Results of these and other runs suggest that a wall conditioning process was occurring. After this conditioning

process,  $O_3$  production rate was less erratic. In the second run, peak steady state  $O_3$  concentration was about 115 pphm in an irradiation time of about 40 minutes. Also on the same figure is shown the ozone decay (dark circled data) when irradiation is stopped. For the two runs the decay was an exponential one. Decay rates for the first and second run were about  $0.011 \text{ min}^{-1}$  and  $0.015 \text{ min}^{-1}$ , respectively. These results indicate that the  $O_3$  decay may not be due entirely to wall reaction alone, otherwise one would expect the decay rate for the second run (after wall conditioning) would be less than that for the first run.

#### Effect of Addition of NO to "UPC" Air on $O_3$ Production

The effect of adding varying amounts of NO to "UPC" air on  $O_3$  production is shown in Figs. 3, 4, and 5. For purpose of comparison, an  $O_3$  production reference curve for air alone is shown in the three figures. This reference curve is an average of some  $O_3$  production data for air alone obtained just before and after these tests involving addition of NO were made. Figure 3 shows that when air containing an initial concentration of 30 pphm NO (as measured by the  $NO_x$  analyzer), is irradiated, the  $O_3$  production is affected only slightly. Unfortunately, the  $NO_x$  analyzer during these three runs could measure oxides of nitrogen as total  $NO_x$  only. It is interesting to note that the total  $NO_x$  decreased almost linearly with time.

Figure 4 shows that when the initial NO is about 65 pphm, the NO inhibiting effect on  $O_3$  production is increased as compared to the results with 30 pphm NO (Fig. 3). The  $O_3$  production delay time is about 20 minutes. This delay time is defined as being the time duration from time zero to a time at which the  $O_3$  production rate is about 0.2 pphm per minute. The interesting thing here is that this inhibiting effect is only temporary, since the total  $NO_x$  in the chamber is again decreasing almost linearly with time.

When the initial NO is 128 pphm (Fig. 5), the NO inhibiting effect is increased to the extent that the delay time is now about 80 minutes. Again the total  $NO_x$  decreases with time, but in a more nonlinear manner.

A fourth run, in which the NO was about 60 pphm, was made when the  $\text{NO}_x$  analyzer was fully operational. These results are shown in Fig. 6. The  $\text{O}_3$  reference curve for "UPC" air alone was obtained a day before this run. These results agree reasonably well with those shown in Fig. 4, in which the added NO was about 65 pphm. The  $\text{NO}_x$  measurements shown in Fig. 6 can now explain partly why the NO inhibiting effect is only temporary. Measurements of NO and  $\text{NO}_2$  indicate that NO is rapidly consumed, or converted to  $\text{NO}_2$  (by reaction with  $\text{O}_3$ ), and that no NO was regenerated. This suggests that for our experimental condition, both reaction VI ( $\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}$ ) and reaction VII ( $\text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2$ ) were inoperative in recycling NO. The gradual decrease in  $\text{NO}_2$  may indicate further reactions involving  $\text{NO}_2$  to form  $\text{N}_2\text{O}_5$ , dinitrogen pentoxide. This  $\text{N}_2\text{O}_5$  can, perhaps, be removed by a heterogeneous reaction with trace moisture on the chamber walls to form  $\text{HNO}_3$ , nitric acid (Gay and Bufalini (1971)). These reactions will be discussed later in more detail.

Figure 7 is a summary curve showing the effect of varying amounts of initial NO on  $\text{O}_3$  production. These experiments indicate that the observed inhibiting effect of NO is due mostly to gas phase chemical reactions.

#### Effect of Addition of CO, NO, and $\text{H}_2\text{O}$ to

##### "UPC" Air on $\text{O}_3$ Production

The next series of tests consisted of determining the effect on  $\text{O}_3$  production of addition of some initial CO and  $\text{H}_2\text{O}$  to "UPC" air containing some NO. Prior to these runs involving CO and  $\text{H}_2\text{O}$  addition, a run was made to determine the effect on  $\text{O}_3$  production of adding initially 76 pphm NO and about 1200 ppm  $\text{H}_2\text{O}$  to air. This result is shown in Fig. 8. On this same figure is another reference curve for air alone, obtained a day prior to the air + NO +  $\text{H}_2\text{O}$  run. As expected, when some NO is present, a delay in  $\text{O}_3$  production is observed. Unexpectedly, the  $\text{O}_3$  production eventually exceeds that for air alone temporarily. The delay time is about 25 minutes, which is about the same

as that when the initial NO was 60 or 65 pphm in dry air (Figs. 4 and 6).

The effect of initial addition of 50 ppm CO to air containing about 75 pphm NO and about 1200 ppm H<sub>2</sub>O is shown in Fig. 9. Two comparison curves are presented, one for "UPC" air alone and the other for "UPC" air containing some added NO and H<sub>2</sub>O. The addition of CO results in a slight decrease in O<sub>3</sub> production delay time to about 21 minutes versus 25 minutes in the absence of CO. No NO<sub>x</sub> measurements were obtained for this run due to a breakdown in the NO<sub>x</sub> analyzer.

The effect of adding initially 100 ppm CO to "UPC" air containing 60 pphm NO and about 1200 ppm H<sub>2</sub>O is shown in Fig. 10. For this run the NO<sub>x</sub> analyzer was fully operational, and NO and NO<sub>2</sub> measurements were made. These results showed that when more CO is added, the delay time is now reduced to about 9 minutes versus 21 minutes when the added CO was 50 ppm. In addition, the peak O<sub>3</sub> production was increased to about 162 pphm. This additional O<sub>3</sub> production may be attributed to the action of photosmog type reactions occurring in the reaction chamber. NO<sub>x</sub> measurements showed that the NO<sub>x</sub> decay is now an exponential one, whereas in the absence of CO, the NO<sub>x</sub> decay was more linear and slower (see Figs. 3 to 6). Peak NO<sub>2</sub> formation was reached in about 25 minutes versus 50 minutes when no CO was present (Fig. 6). Again no NO was regenerated just as in the work involving addition of NO alone.

When the CO concentration was increased to about 220 ppm, the effect on O<sub>3</sub> production is shown in Fig. 11. Delay time is now further reduced to about 1 minute and O<sub>3</sub> production of about 172 pphm was reached. The NO<sub>x</sub> measurements indicated that both NO and NO<sub>x</sub> decays were accelerated, and peak NO<sub>2</sub> concentration occurred in about 14 minutes instead of 25 minutes, when 100 ppm CO was added. It was observed again that no NO was regenerated.

Figure 12 is a summary plot showing the effect of additions of varying amounts of CO to counteract the NO inhibiting effect on O<sub>3</sub> production. These experimental results indicate that CO and H<sub>2</sub>O addition can counteract the NO destruction of O<sub>3</sub> and result in higher O<sub>3</sub> concentration in the chamber.

## COMPARISON OF EXPERIMENTAL AND THEORETICAL RESULTS

### Results With Pure Air

The steady-state analysis with the simple Chapman mechanism (reactions I-IV) mentioned previously shows that these reactions alone cannot account for the observed leveling off of the  $O_3$  concentration in the chamber. An additional destruction reaction for  $O_3$  has to be used in the chemical mechanism. This single reaction is used to represent a destruction process which may be a combination of surface and gas phase processes. For computations with our general chemical kinetics program, both simple first order and second order kinetics were used for the additional destruction reaction to see if either assumption would be more consistent with the experimental results. For all computations air was assumed to be 79.05 mole percent  $N_2$  and 20.95 percent  $O_2$ .

The exact intensity versus wavelength distribution of our solar simulator light source was not known below 250 nm. Thus, none of the photochemical rate constants could be computed exactly. Therefore, for all computations, reasonable literature values were used at the start. When necessary they were changed within reasonable limits to give agreement between experimental and computed results. The steady-state analysis with the Chapman mechanism shows that reaction I, the oxygen photolysis, completely controls the rate of formation of  $O_3$  in the early stages of the reaction. Several preliminary computations established that any computed  $O_3$  concentration profile is controlled only by two rate constants. These are  $J_1$ , for the oxygen photolysis, and the rate constant for the assumed extra  $O_3$  destruction reaction in addition to reactions III and IV. These last two reactions can in no way account for the leveling off of the  $O_3$  concentration in our experiment. A series of computations was done with two different destruction reactions, using each separately. The overall destruction reaction used is either



or



In performing the computations, the value of  $J_1$  was chosen to match the initial slope of the  $\text{O}_3$  concentration versus time curve. Then the value of  $k_{D_1}$  or  $k_{D_2}$  was chosen to agree with the final portion of the concentration profile. In this analysis a computed curve is chosen to match experimental data in a semiquantitative way. It is a curve which, in the authors' judgement, closely represents the trend and magnitudes of the experimental data. This technique calibrates our system and these rate constants can then be used to analyze the experimental results in the presence of various amounts of pollutants. Inasmuch as there is a small effect of diffusion of ozone from the lighted volume of the reaction chamber to the wall, the rate constants found in this procedure also include any diffusion effects.

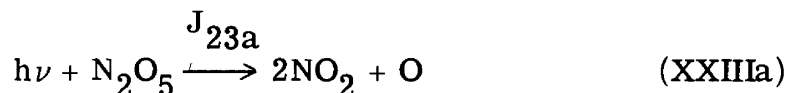
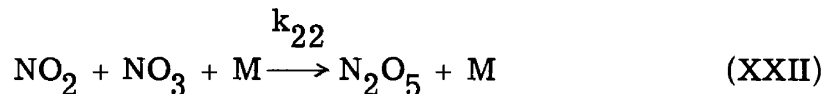
Computations were also made to match the experimentally observed ozone decay in our chamber. This was done to obtain preliminary values of  $k_{D_1}$  and  $k_{D_2}$ . Figure 13 shows data for two experiments where ozone decay was observed. The solar simulator was turned off after the ozone concentration reached a steady state value of 120 pphm. The mechanism used to compute the expected decay curve consists of reactions II, IV, and either  $\text{D}_1$  or  $\text{D}_2$ . The value of  $k_{D_1}$  or  $k_{D_2}$  was found to completely control the ozone decay curve. The two curves in Fig. 13 show the best results obtained using either reaction  $\text{D}_1$  or  $\text{D}_2$ . The values obtained are  $k_{D_1} = 4 \times 10^{-4} \text{ sec}^{-1}$  and  $k_{D_2} = 5 \times 10^6 \text{ cm}^3/\text{mole-sec}$ . The curve using reaction  $\text{D}_1$  (unimolecular decomposition) follows the trend of the experimental data somewhat better than the curve using the bimolecular destruction, reaction  $\text{D}_2$ .

The ozone destruction mechanism may not be exactly the same with the light on as with it off. Therefore, both reactions  $D_1$  and  $D_2$  were used (separately) in two series of computations to match the ozone formation experimental results. The value of  $k_{D_1}$  or  $k_{D_2}$  was first set at the value given above. Then the oxygen photolysis rate constant  $J_1$  was changed to obtain good agreement between experimental and computed results for the beginning of the reaction. The  $k_{D_1}$  or  $k_{D_2}$  value was then varied slightly to match the experimental data for the end of the reaction. Figure 14 shows the results of these trials. The data points are for three different ozone formation experiments performed over a 2-month period before the chamber surface was exposed to any pollutant. The two curves are the computed curves obtained using the two different destruction reactions,  $D_1$  and  $D_2$ . Rate constants used for these computations are  $J_1 = 1 \times 10^{-9} \text{ sec}^{-1}$ ,  $k_{D_1} = 3 \times 10^{-4} \text{ sec}^{-1}$ , and  $k_{D_2} = 4 \times 10^6 \text{ cm}^3/\text{mole-sec}$ . The two curves are very much the same. Either reproduces the experimental data quite well. These computations do not distinguish whether a first or second order  $O_3$  destruction reaction occurs in the reaction chamber. Therefore, for the computations in the presence of pollutants, both reactions were considered. All computations were performed first using reaction  $D_1$  and then repeated using reaction  $D_2$ . The rate constants used for all reactions considered in this work are listed in Table I.

### Results With Nitric Oxide

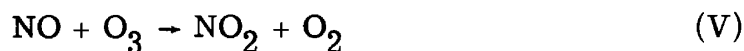
Computations were performed for the case of nitric oxide added to dry air. The first mechanism used consists of reactions I through XI plus reaction  $D_2$ . The computed results did not agree qualitatively or quantitatively with the experimental results. The ozone concentration leveled off at a value much lower than that observed experimentally. No rate variations within estimated uncertainties changed these qualitative results. Adding two additional reactions, however, had a significant

effect on the computed ozone profile. These reactions, which involve nitrogen pentoxide,  $\text{N}_2\text{O}_5$ , are



A comparison of computed and experimental results using reactions XXII and XXIIIa is shown in Fig. 15(a) and (b). Part (a) shows computations using destruction reaction  $\text{D}_1$  and part (b) shows computations using reaction  $\text{D}_2$ . For either reaction, the computed curves follow the qualitative trends of the experimental curves. For 30 pphm of NO, the computed delay in  $\text{O}_3$  formation is longer than the observed delay. For the higher initial NO concentrations, the computed delay is shorter than that observed.

Analysis of the rates of formation and destruction of ozone by individual reactions shows that different ones are important at different times. At the beginning of the reaction the  $\text{O}_3$  formed by reaction II is destroyed primarily by the reaction



As ozone is built up it is also destroyed by



Another destruction reaction that is relatively unimportant compared to the previous two reactions is





The additional destruction reactions  $D_1$  and  $D_2$  are even less important than reaction VIII in destroying  $O_3$  at the start of the reaction.

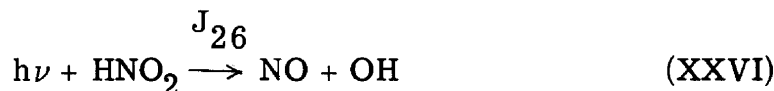
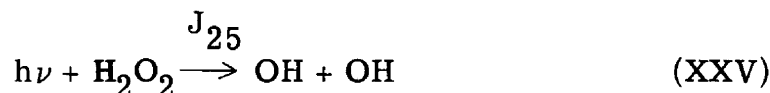
At the end of the reaction,  $O_3$  concentration levels off because reaction II is balanced primarily by the effect of the photolysis destruction, reaction III. The destruction reaction  $D_1$  or  $D_2$  has a much smaller effect in determining the final  $O_3$  level for this system than for the pure air system. These computations support the previous interpretation of the experimental results. It was stated previously that the experimental results should be representative of homogeneous gas phase reaction in the chamber. The effect of the chamber walls is small during most of the reaction time.

Figure 16 shows several computed species concentration histories for the air + 65 pphm nitric oxide case. Comparison with the experimental curves shown in Fig. 6 indicates good qualitative agreement in general. Nitric oxide is rapidly converted to  $NO_2$ . Nitrogen dioxide concentration peaks at about the maximum slope of the ozone concentration curve, and then decreases. The experimental decrease of  $NO_2$  (Fig. 6) is slower than that computed because the  $NO_2$  measurement probably includes higher oxides of nitrogen. Computations show that  $N_2O_5$  is formed slowly after about 20 minutes and increases to a steady-state value.

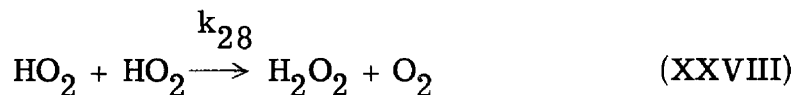
The preceding discussion refers to computations using reaction XXIIIa, the  $N_2O_5$  photolysis reaction giving the products  $2NO_2 + O$ . All results are essentially the same when the computations are repeated using reaction XXIIIb, which gives the products  $NO_2 + NO_3$ . The computed concentration profiles were compared with those of the early computations, without any  $N_2O_5$  reactions present. It was observed that  $NO_2$  concentration remains high during most of the reaction when it cannot react to form  $N_2O_5$ . If  $NO_2$  concentration stays high, computations show that it will destroy  $O_3$  by the direct  $NO_2 + O_3$  reaction. The present analysis gives no information about the products of the  $N_2O_5$  photolysis.

Results With NO, CO, and H<sub>2</sub>O

The mechanism for O<sub>3</sub> chemistry in the presence of CO, NO, and H<sub>2</sub>O includes reactions I to XXIII plus reactions which provide OH radicals. The latter are necessary for starting the chain (reactions XII to XV) which converts NO to NO<sub>2</sub> without the destruction of O<sub>3</sub>. The following photolysis reactions were used as the source for OH:



Hydrogen peroxide, H<sub>2</sub>O<sub>2</sub>, is formed by the reaction



Rate constants for the photolysis reactions were chosen to give satisfactory agreement with the experimental results. The values used are generally within a factor of 4 of those given by McConnell and McElroy (1973) for an altitude of 80 km. However, J<sub>24</sub>, the H<sub>2</sub>O photolysis rate constant, was taken as 1/10th of their value. Computations show that the two important sources of OH in our mechanism are the H<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub> photolyses.

The rate constants used in the dry air plus NO computations were not changed for the computations with CO and H<sub>2</sub>O also present. Computed results were found to be only slightly different using O<sub>3</sub> destruction

reaction  $D_1$  from results using reaction  $D_2$ . Inasmuch as the 10 percent higher final  $O_3$  concentration using  $D_2$  was more in agreement with experiment, the computations to be discussed use reaction  $D_2$ .

Figure 17 shows both the experimental and typical computed results for  $O_3$  production in air containing 50 ppm CO, 75 pphm NO, and 1200 ppm  $H_2O$ . Also shown for comparison are experimental and computed  $O_3$  concentration curves for "UPC" air + 65 pphm NO added initially. These last two curves are the same ones shown in Fig. 15(b). There is poor quantitative agreement between experimental and computed curves in the presence of CO and  $H_2O$ . However, the computed results show the same qualitative effect of CO that is observed experimentally. The computed delay in  $O_3$  formation is much less in the presence of CO and  $H_2O$ . It is clear that the computations do not fully explain the chemical reaction in the presence of CO and  $H_2O$ . The slope of the main portion of the computed curve is much lower than that for the experimental curve. Moreover, the steady state  $O_3$  concentration is also lower on the computed curve. Another problem is the failure of the computations to show increased effectiveness of higher CO initial concentrations. The computed results for 200 ppm CO present show a significantly smaller difference from the results for 50 ppm CO than is observed experimentally. The qualitative trend is shown, but there is no quantitative agreement. Many rate constant variations showed that the actual delay in  $O_3$  formation is quite sensitive to the rate constants  $J_{24}$  and  $J_{25}$  for photochemical formation of OH radical. However, for all perturbations of other rate constants within their estimated uncertainty, the slope of the main portion of the  $O_3$  concentration curve and the final  $O_3$  level were changed only slightly.

One final point concerning the reactions of  $NO_2$  formed from the original NO, should be mentioned. We have discussed earlier the possibility of the removal of higher oxides of nitrogen from the gas phase as  $HNO_3$  condensed on the chamber walls (Gay and Bufalini (1971)). This idea provides one possible reason for the disagreement between computed and experimental  $O_3$  production. The computations do not allow the removal of higher oxides of nitrogen from the gas phase.

Our reaction mechanism gives only a relatively small amount of indirect conversion of  $\text{N}_2\text{O}_5$  to  $\text{HNO}_3$  via reactions XXIII and XX. This is certainly unrealistic. Our gas phase mechanism does not properly explain the subsequent reactions of  $\text{NO}_2$ . Additional computations must be done to better explain our experimental results.

### CONCLUDING REMARKS

The main concern about the effect of nitric oxide emission in the stratosphere has been its possible long lasting destruction of ozone. Many papers (e.g., Johnston (1971), Westenberg (1972)) have predicted that NO destroys ozone catalytically, i. e., without itself being destroyed. These conclusions were based on approximate steady state analyses and the assumption that all the  $\text{NO}_2$  formed by reaction V would be photolyzed back to NO by reaction VI. The present laboratory scale experiment indicates that NO is destroyed while destroying  $\text{O}_3$ . The  $\text{O}_3$  formation reaches its usual level (in the absence of pollutants) soon after most of the NO has been converted to  $\text{NO}_2$  and other oxides of nitrogen. Even though  $\text{NO}_2$  is partially photolyzed back to NO, this reaction also produces oxygen atoms. These, along with the O atoms from the photolysis of  $\text{O}_2$ , form more ozone than the regenerated NO can destroy. The computations for dry air with NO added show that NO is destroyed much faster by the  $\text{NO} + \text{O}_3$  reaction than it is regenerated by  $\text{NO}_2$  photolysis in the early stages of the reaction. In the latter part of the reaction NO concentration becomes quite low. Then the NO concentration stays at this low level because its formation by  $\text{NO}_2$  photolysis (and the reaction  $\text{O} + \text{NO}_2 \rightarrow \text{NO} + \text{O}_2$ ) is exactly balanced by its destruction in the  $\text{NO} + \text{O}_3$  reaction. At this time the  $\text{O}_3$  forming reactions cause the  $\text{O}_3$  level to build up to its usual level in the absence of NO.

The effect of CO and  $\text{H}_2\text{O}$ , which increases  $\text{O}_3$  concentration in the present experiment, is not completely understood. Since these products are present, along with NO, in engine exhausts, the matter of equilibrium  $\text{O}_3$  concentration in the presence of engine discharges is still uncertain.

An important question is whether our laboratory results can be applied to low pressure conditions. To partly answer this question, the experiments and the theoretical computations just described will be repeated at reduced pressures, down to about 0.3 atm. The latter pressure is the expected lower limit, based on preliminary tests of our modified  $O_3$  analyzer. If the theoretical modelling is successful at this reduced pressure, the same chemical mechanism will be used for theoretical computations at stratospheric pressures. The attempt will be made to predict the trend of  $O_3$  formation in the presence of pollutants down to 0.05 atm. The ratios of the various pollutants will be adjusted to simulate upper atmospheric concentrations.

#### REFERENCES

- Baulch, D. L., D. D. Drysdale and A. C. Lloyd, 1969: High Temperature Reaction Rate Data. Rept. 3, Dept. Phys. Chem., Leeds Univ.
- Bittker, D. A., and V. J. Scullin, 1972: General Chemical Kinetics Computer Program for Static and Flow Reactions, With Application to Combustion and Shock-Tube Kinetics. NASA Tech. Note D-6586, 187 pp.
- Crutzen, P. J., 1972: The Photochemistry of the Stratosphere with Special Attention Given to the Effects of  $NO_x$  Emitted by Supersonic Aircraft. Proc. Survey Conf. on Climatic Impact Assessment Program, Feb. 15-16, pp. 80-89.
- Davis, D. D., 1972: Recent Kinetic Measurements on Reactions of  $O(^3P)$ , H and  $HO_2$ . Proc. Sec. Conf. on Climatic Impact Assessment Program. Nov. 14-17, pp. 126-143.
- DeMore, W. B., 1973: Rate Constants for Reactions of Hydroxyl and Hydroperoxyl Radicals with Ozone. *Sci.*, 180, pp. 735-737.
- Dütsch, H. U., 1972: The Present Status of Ozone Research: Photochemistry and Observations. Proc. Sec. Conf. on Climatic Impact Assessment Program, Nov. 14-17, pp. 106-113.

- Garvin, D., ed., 1973: Chemical Kinetics Data Survey V. Sixty-six Contributed Rate and Photochemical Data Evaluations on Ninety-Four Reactions. Rept. NBSIR 73-206, National Bureau of Standards.
- Garvin, D. and R. F. Hampson, eds., 1974: Chemical Kinetics Data Survey VII. Tables of Rate and Photochemical Data for Modelling of the Stratosphere (Revised). Rept. NBSIR 74-430, National Bureau of Standards.
- Gay, B. W., Jr., and J. J. Bufalini, 1971: Nitric Acid and the Nitrogen Balance of Irradiated Hydrocarbons in the Presence of Oxides of Nitrogen. *Env. Sci. Techn.*, 5, pp. 422-425.
- Hampson, R. F., ed., 1972: Chemical Kinetics Data Survey I. Rate Data for Twelve Reactions of Interest for Stratospheric Chemistry. Rept. 10 692, National Bureau of Standards.
- Heicklen, J., K. Westberg and N. Cohen, 1969: Conversion of NO to NO<sub>2</sub> in Polluted Atmospheres. Chemical Reactions in Urban Atmospheres. American Elsevier Pub. Co., pp. 55-58.
- Johnston, H. S., 1971: Reduction of Stratospheric Ozone by Nitrogen Oxide Catalysis for Supersonic Transport Exhaust. *Sci.*, 173, pp. 517-22.
- Kellogg, W. W., chairman, Work Group on Climatic Effects, 1970: Man's Impact on the Global Environment: Report of the Study of Critical Environmental Problems, M. I. T. Press, pp. 100-112.
- Leighton, Philip A., 1961: Photochemistry of Air Pollution. Academic Press.
- McConnell, J. C., and M. B. McElroy, 1973: Odd Nitrogen in the Atmosphere. *J. Atm. Sci.*, 30, pp. 1465-80.
- Simonaitis, R. and J. Heicklen, 1972: The Reaction of OH With NO<sub>2</sub> and Deactivation of O(<sup>1</sup>D) by CO. *Int. J. Chem. Kinetics*, 4, pp. 529-40.

- Schofield, K., 1967: An Evaluation of Kinetic Rate Data for Reactions of Neutrals of Atmospheric Interest. Planet. Space Sci. 15, pp. 643-70.
- Westberg, K. and N. Cohen, 1971: Carbon Monoxide: Its Role in Photochemical Smog. Sci., 171, pp. 1013-1015.
- Westenberg, A. A., 1972: Effect of  $\text{NO}_x$  on Stratospheric Ozone. Tech. Memo. TG 1186, Johns Hopkins Univ. Applied Physics Laboratory.

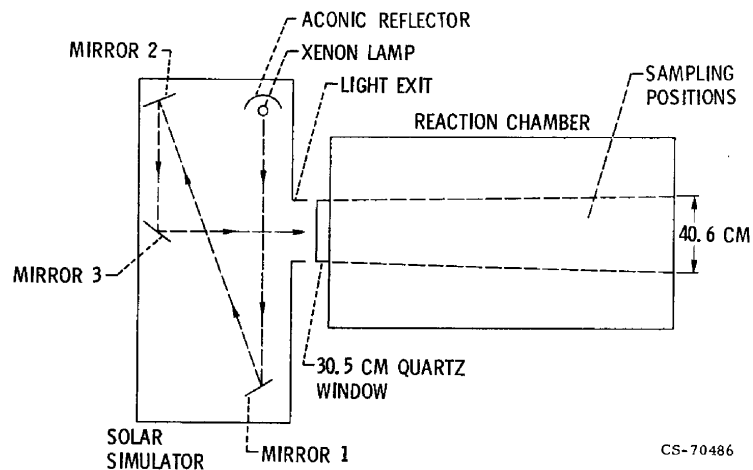


Figure 1. - Simulator and reaction chamber.

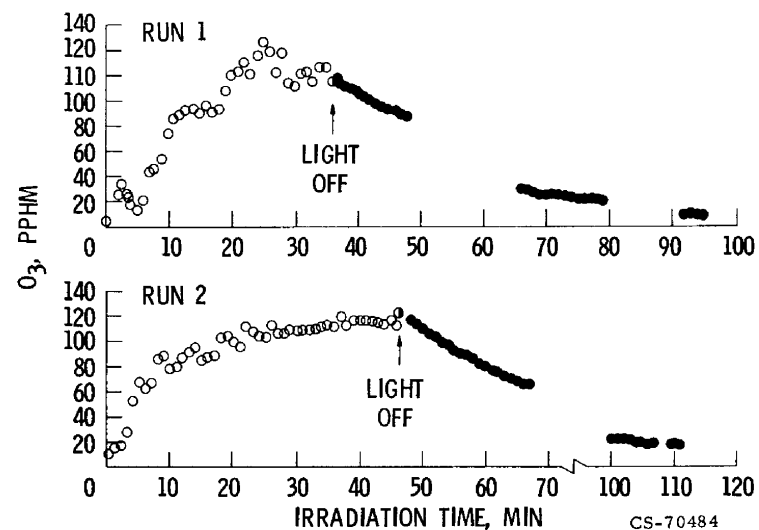
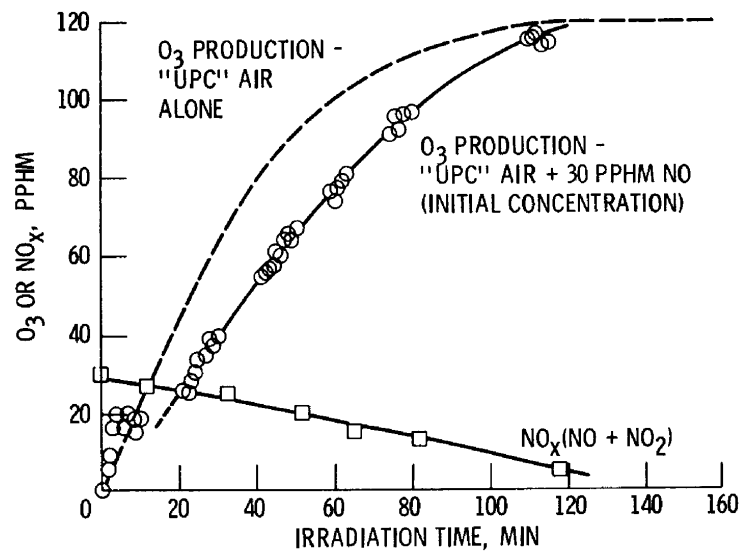
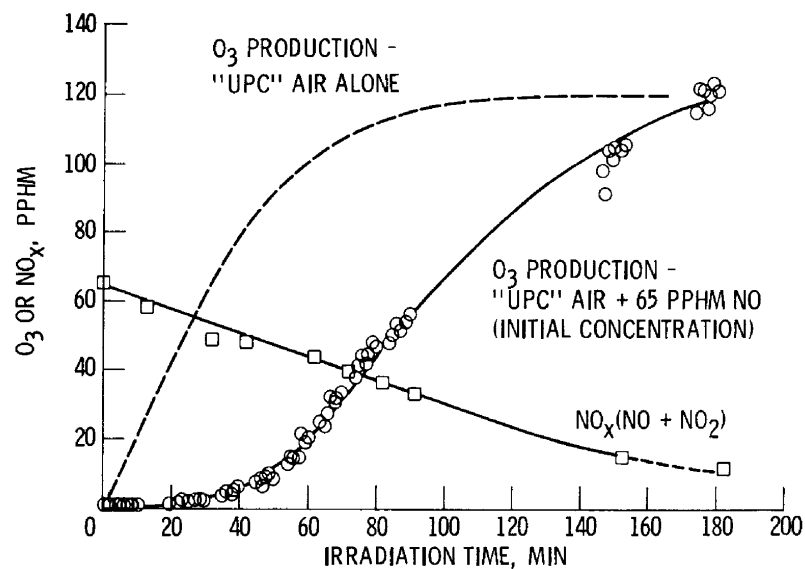


Figure 2. - Ozone production for "UPC" air.

Figure 3. - Ozone production for "UPC" air containing 30 pphm  $NO$ .Figure 4. - Ozone production for "UPC" air containing 65 pphm  $NO$ .



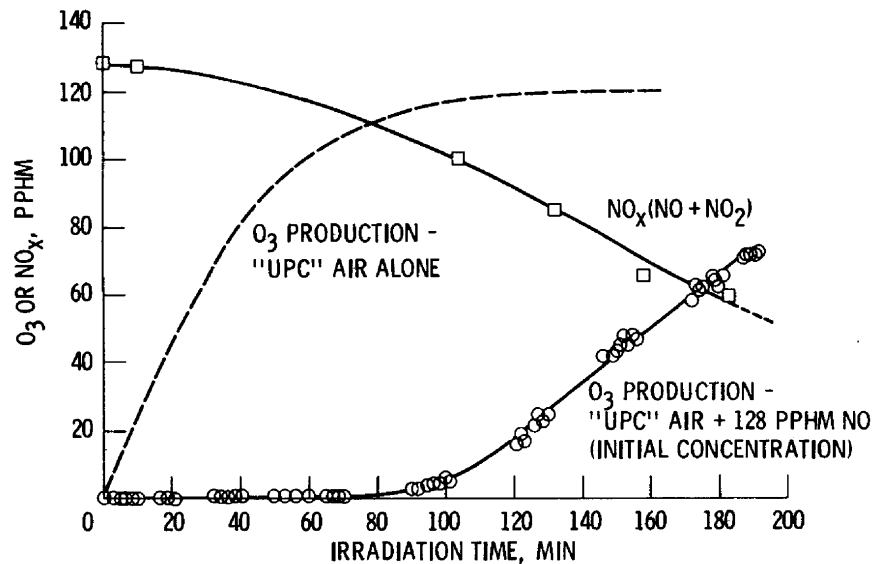


Figure 5. - Ozone production for "UPC" air containing 128 pphm NO.

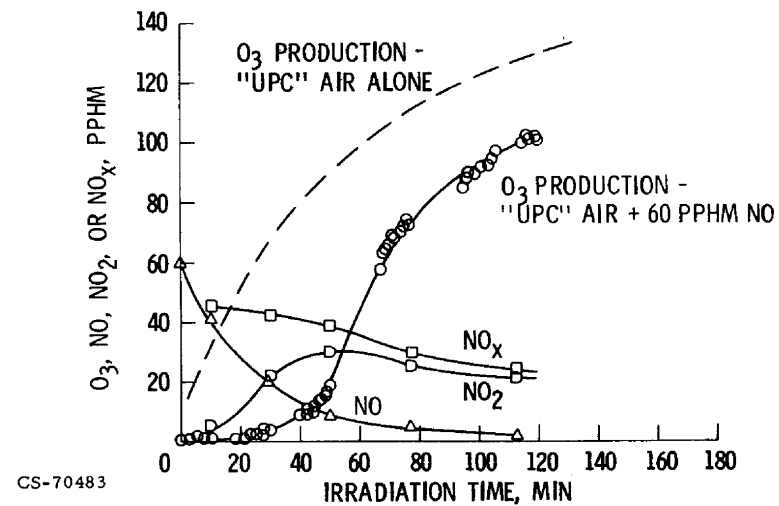


Figure 6. -  $O_3$  production for "UPC" air containing 60 pphm NO.

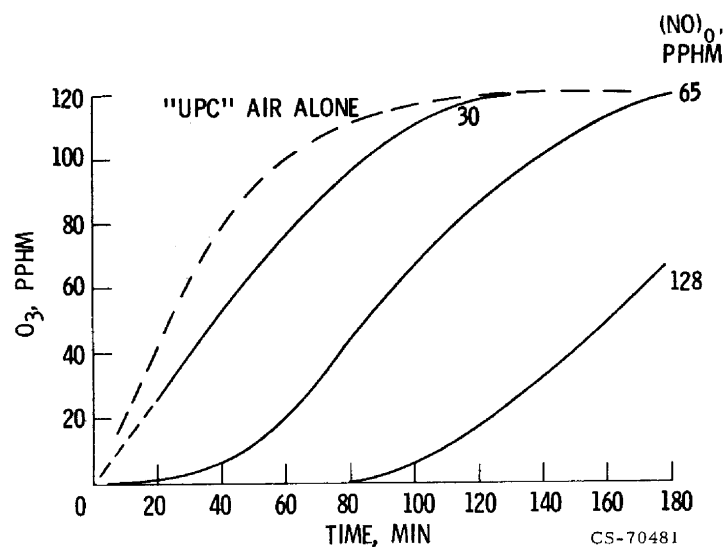


Figure 7. -  $O_3$  production for "UPC" air containing various initial amounts of NO.

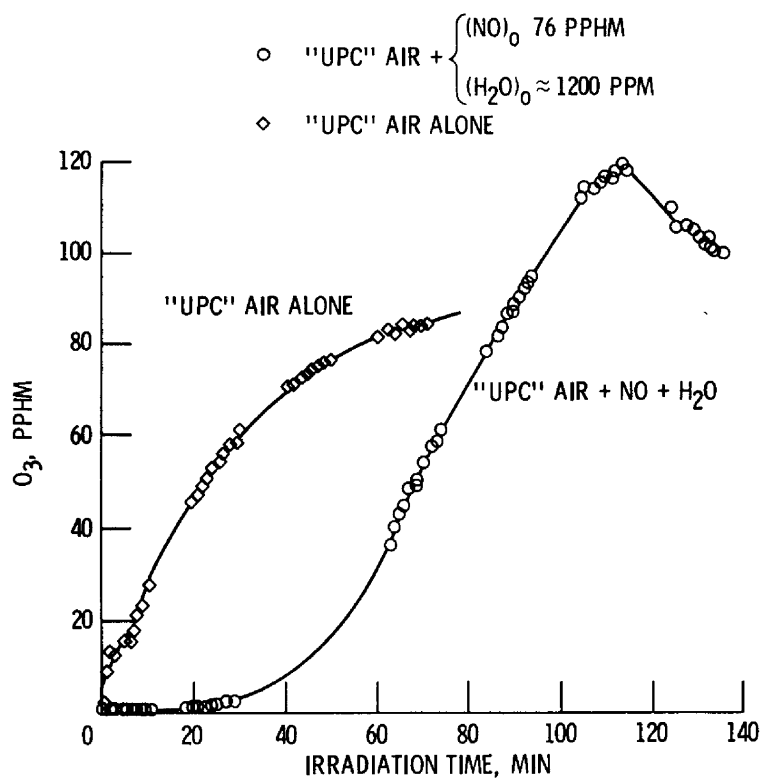


Figure 8. - Ozone production for "UPC" air containing 76 pphm NO and 1200 ppm H<sub>2</sub>O.

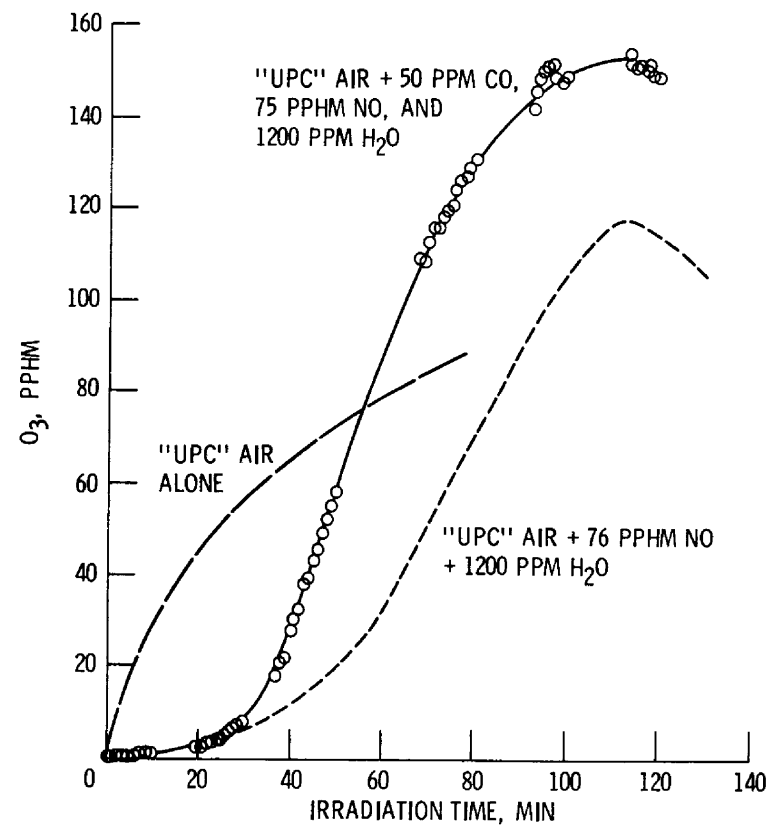


Figure 9. - Ozone production for "UPC" air containing about 50 ppm CO, 75 pphm NO, and 1200 ppm H<sub>2</sub>O.

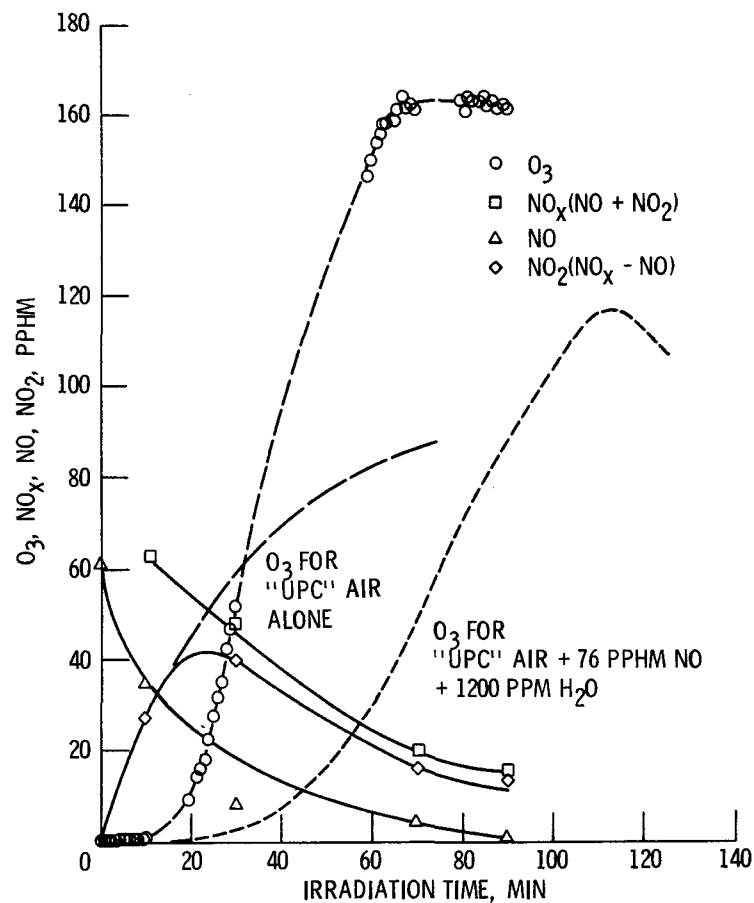


Figure 10. - Ozone production for "UPC" air containing about 100 ppm CO, 60 pphm NO, and 1200 ppm  $H_2O$ .

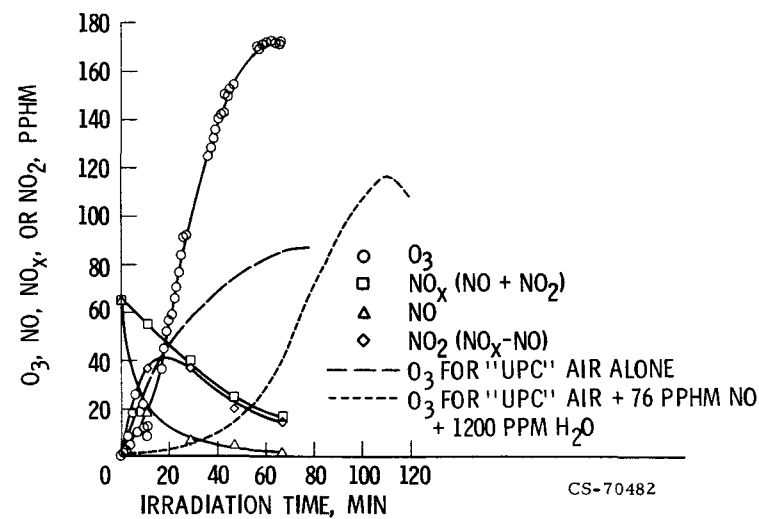


Figure 11. - Ozone production for "UPC" air containing about 220 ppm CO, 65 pphm NO, and 1200 ppm  $H_2O$ .

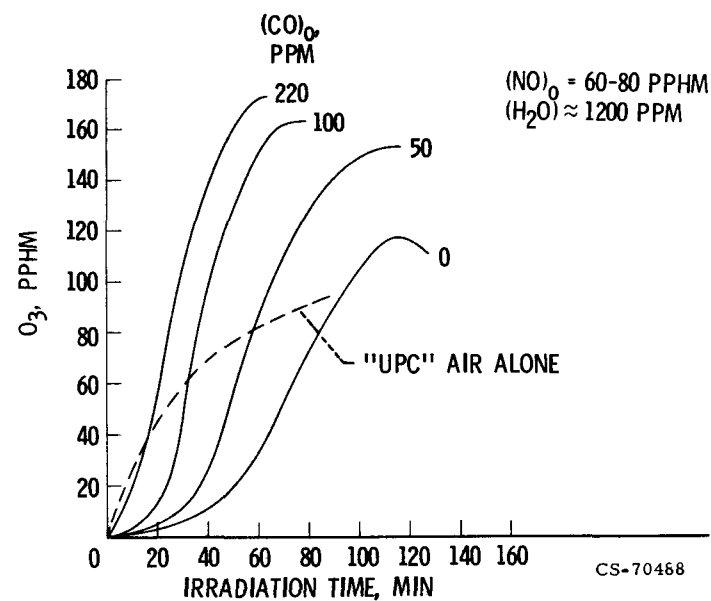


Figure 12. - Ozone production when various amounts of CO are added to "UPC" air containing some NO and  $H_2O$ .

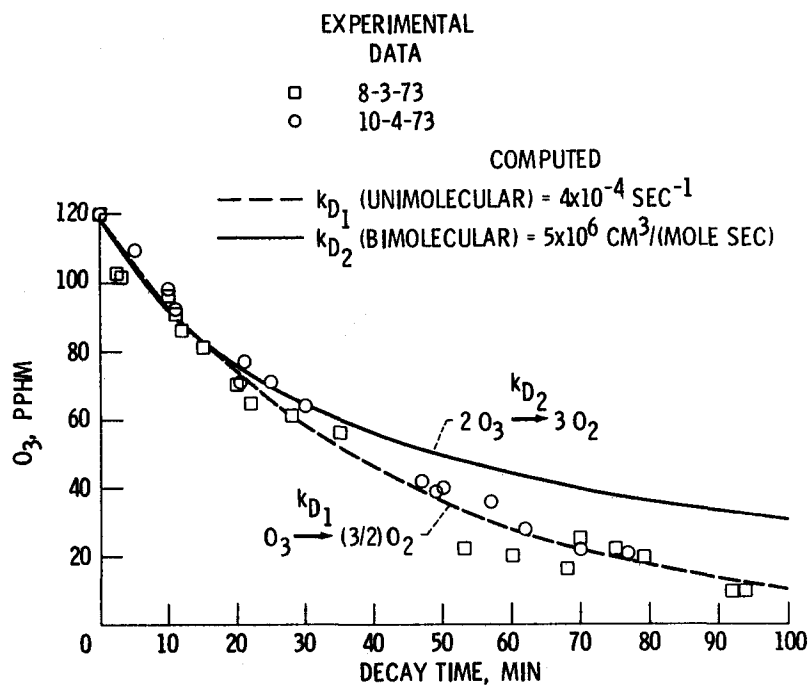


Figure 13. - Ozone destruction in "UPC" air; experimental and theoretical.

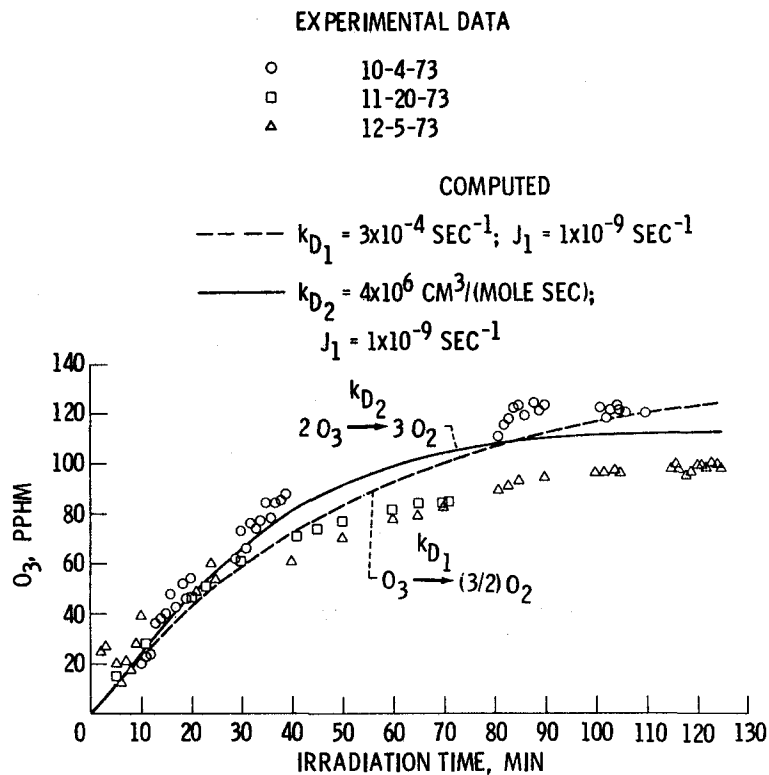


Figure 14. - Ozone formation in "UPC" air; experimental and theoretical.

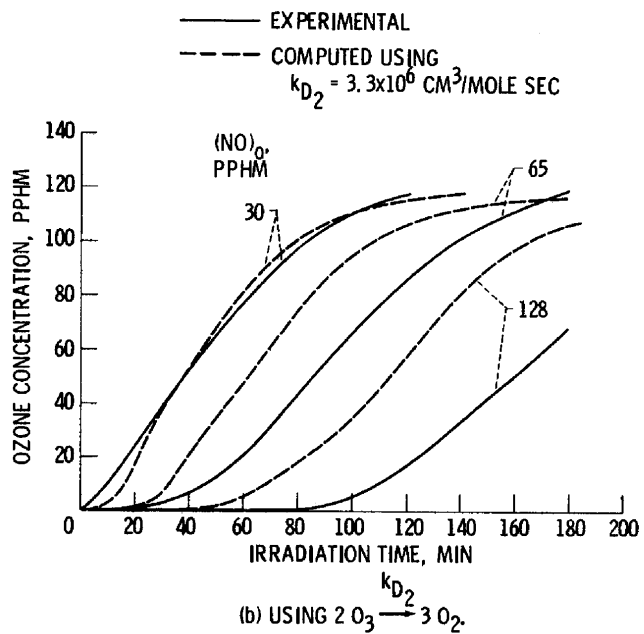
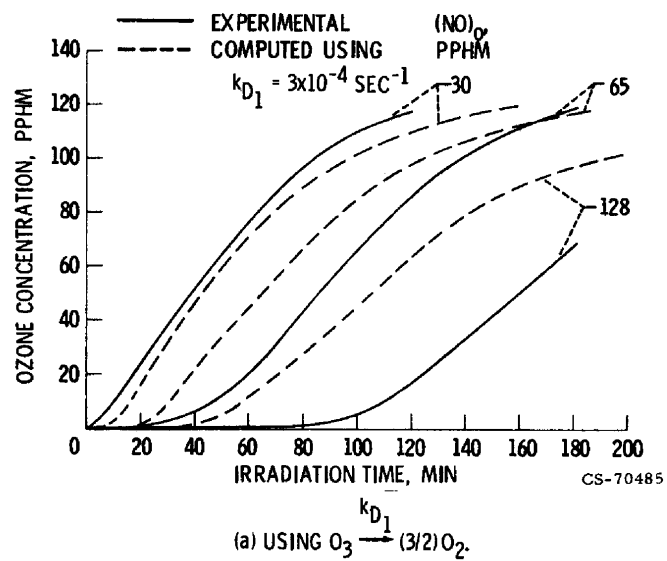


Figure 15. - Comparison of experimental and theoretical ozone formation in air + nitric oxide mixtures.

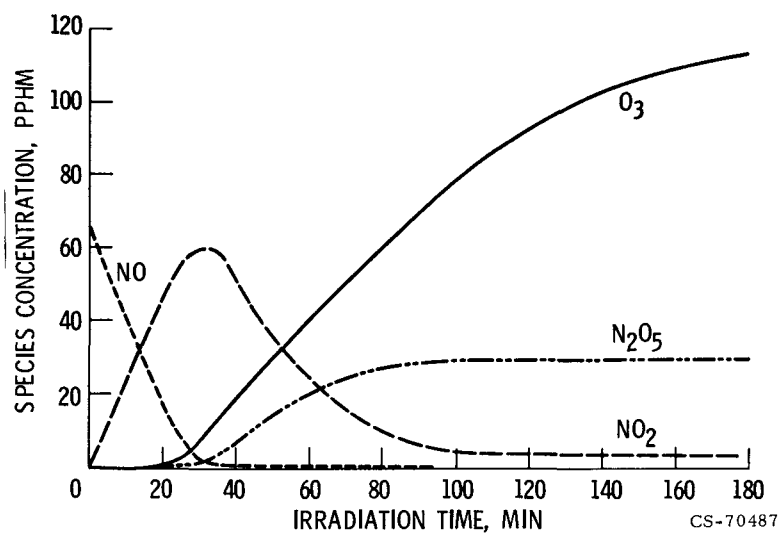


Figure 16. - Species concentration vs. time for irradiation of air + 65 pphm nitric oxide; computed results using uni-molecular destruction reaction,  $O_3 \rightarrow (3/2)O_2$ .

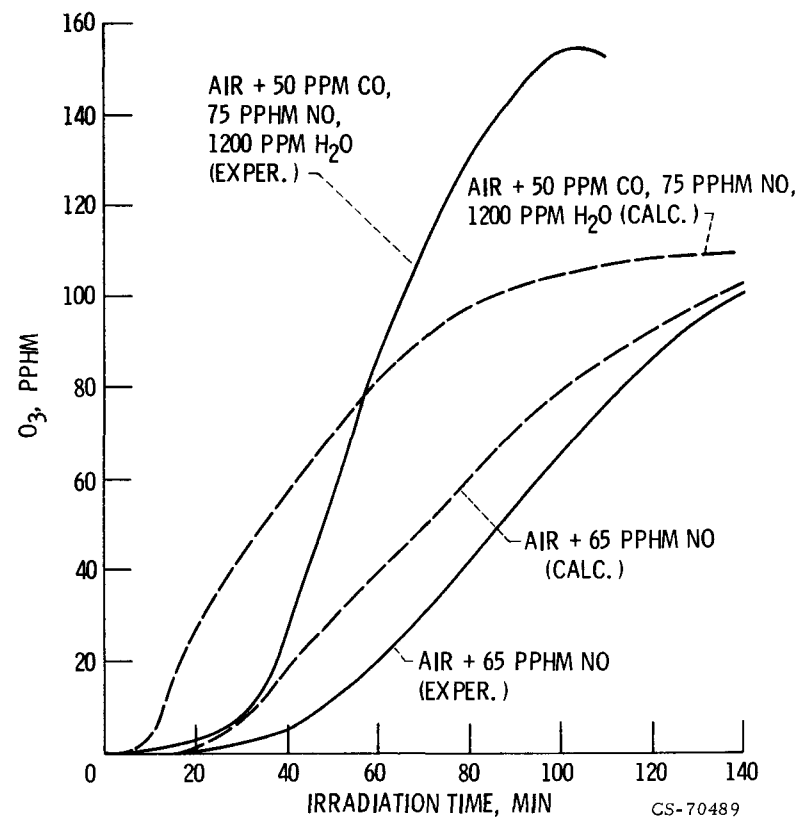


Figure 17. - Effect of CO, NO, and  $H_2O$  on  $O_3$  formation.

TABLE I. - CHEMICAL REACTIONS AND RATE CONSTANTS

Number	Reaction	Preexponential factor, * A	Temperature exponent, * n	Activation energy, * kcal/mole	References
I	$h\nu + O_2 \rightarrow O + O$	$1 \times 10^{-9}$	0.0	0.0	See text
II	$O + O_2 + M \rightarrow O_3 + M$	$3.83 \times 10^{13}$		-1.01	Garvin and Hampson (1974) M = N <sub>2</sub>
III	$h\nu + O_3 \rightarrow O + O_2$	$3.55 \times 10^{-3}$		.0	Westenberg (1972) <sup>†</sup>
IV	$O + O_3 \rightarrow O_2 + O_2$	$1.1 \times 10^{13}$		4.57	Garvin and Hampson (1974)
V	$NO + O_3 \rightarrow NO_2 + O_2$	$5.5 \times 10^{11}$		2.39	Garvin and Hampson (1974)
VI	$h\nu + NO_2 \rightarrow NO + O$	$1 \times 10^{-3}$		.0	McConnell and McElroy (1973) <sup>†</sup>
VII	$O + NO_2 \rightarrow NO + O_2$	$5.5 \times 10^{12}$		.0	Garvin and Hampson (1974)**
VIII	$NO_2 + O_3 \rightarrow NO_3 + O_2$	$3 \times 10^7$		.0	Garvin and Hampson (1974)**
IX	$2NO + O_2 \rightarrow 2NO_2$	$1.2 \times 10^9$		-1.05	Garvin and Hampson (1974)
X	$NO + O + M \rightarrow NO_2 + M$	$9.4 \times 10^{14}$		-1.93	Schofield (1967)
XI	$h\nu + NO_3 \rightarrow NO + O_2$	$1 \times 10^{-3}$		.0	McConnell and McElroy (1973) <sup>†</sup>
XII	$CO + OH \rightarrow CO_2 + H$	$8.7 \times 10^{10}$		.0	Garvin and Hampson (1974)**
XIII	$H + O_3 \rightarrow HO_2 + M$	$1.59 \times 10^{15}$		-1.0	Baulch, et al. (1969) M = Ar <sup>†</sup>
XIV	$NO + HO_2 \rightarrow NO_2 + OH$	$3.6 \times 10^{11}$		.0	Davis (1972) <sup>†</sup> ,**
XV	$H + NO_2 \rightarrow NO + OH$	$2.9 \times 10^{13}$		.0	Garvin and Hampson (1974)**
XVI	$OH + O_3 \rightarrow HO_2 + O_2$	$3 \times 10^{11}$		1.99	Garvin and Hampson (1974) <sup>†</sup>
XVII	$HO_2 + O_3 \rightarrow OH + 2O_2$	$3 \times 10^{10}$		2.49	Garvin and Hampson (1974) <sup>†</sup>
XVIII	$NO + OH + M \rightarrow HNO_2 + M$	$3 \times 10^{16}$		.0	Garvin and Hampson (1974)**
XIX	$OH + HNO_2 \rightarrow H_2O + NO_2$	$8.4 \times 10^{11}$		1.99	Hampson (1972)
XX	$NO_2 + OH + M \rightarrow HNO_3 + M$	$8 \times 10^{16}$		.0	Simonaitis and Heicklen (1972)**
XXI	$OH + HNO_3 \rightarrow H_2O + NO_3$	$8.4 \times 10^{11}$		1.99	Hampson (1972)
XXII	$NO_2 + NO_3 + M \rightarrow N_2O_5 + M$	$1 \times 10^{18}$		.0	Garvin (1973)**
XXIIIa	$h\nu + N_2O_5 \rightarrow 2NO_2 + O$	$1 \times 10^{-4}$		.0	Johnston (1971) <sup>†</sup>
XXIIIb	$h\nu + N_2O_5 \rightarrow NO_2 + NO_3$	$7.7 \times 10^{-5}$		.0	McConnell and McElroy (1973)
XXIV	$h\nu + H_2O \rightarrow H + OH$	$1 \times 10^{-7}$		.0	McConnell and McElroy (1973) <sup>†</sup>
XXV	$h\nu + H_2O_2 \rightarrow OH + OH$	$5.7 \times 10^{-5}$		.0	McConnell and McElroy (1973)
XXVI	$h\nu + HNO_2 \rightarrow NO + OH$	$1.3 \times 10^{-3}$		.0	McConnell and McElroy (1973)
XXVII	$h\nu + HO_2 \rightarrow O + OH$	$3.9 \times 10^{-4}$		.0	McConnell and McElroy (1973)
XXVIII	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	$5 \times 10^{12}$		.99	Garvin and Hampson (1974) <sup>†</sup>

\*Constants in the equation  $k = AT^n \exp(-E_a/RT)$ . Units of k are sec<sup>-1</sup> for photochemical reaction, cm<sup>3</sup>/mole sec for bimolecular reaction; and cm<sup>3</sup>/mole<sup>2</sup> sec for termolecular reaction.

<sup>†</sup>Adjusted from value given in reference.

\*Third body relative efficiencies, N<sub>2</sub>/Ar and O<sub>2</sub>/Ar, for this reaction are taken as 2. A more recent recommended equation (Garvin and Hampson (1974)) gives a value about 20 percent lower at T = 300 K.

\*\*Temperature = 298 K.